# SWERUS-C3 (pH, TA, DIC)

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**Abstract**

This document outlines the procedures followed in the collection and determination of pH, DIC, and TA of seawater samples onboard I/B *Oden* during the 2014 Swedish-Russian-US Arctic Ocean Investigation of Climate-Cryosphere-Carbon Interactions Program, the SWERUS-C3 Program. SWERUS-C3 consists of two 45-day legs, investigating the outer Siberian Shelf and its adjacent slope and ridges. Leg 1 started 5 July in Tromsø, Norway, rotation to Leg 2 20 August in Barrow, AK, USA, ending 4 October in Tromsø, Norway. This document describes the dataset acquired outside the Russian Exclusive Economic Zone and comprise a total of 596 samples from Leg 1 (9 stations) and Leg 2 (30 stations). Seawater was sampled throughout the water column at predefined depths and analyzed onboard within hours (Dickson et al., 2007). All samples were drawn from the rosette by Leif G. Anderson and Ola Holby and were analyzed and processed by Adam Ulfsbo, Sara Jutterström, and Leif G. Anderson (University of Gothenburg, Sweden). Data quality is discussed in this report. Resulting data is correctable through the use of certified reference material (CRM), after which data is deemed to be of reasonably high quality.

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# Contents

# 1 Metadata

**Name of cruise:** SWERUS-C3

**Research vessel:** IB Oden

**Time:** 5 July (Tromsø) to 4 October 2014 (Tromsø)

**Working area:** Outer Siberian Sea Shelf and Slope (East Siberian Sea, Chukchi Sea, Laptev Sea, Lomonosov Ridge)

**Parameters:** Total alkalinity (TA), dissolved inorganic carbon (DIC), pH

**Methods:** Open-cell tritration (TA), coulometric titration (DIC), spectrophotometry (pH

**Samplers:** Leif G. Anderson, Ola Holby (University of Gothenburg, Sweden)

**Analysts:** Adam Ulfsbo, Sara Jutterström, Leif G. Anderson (University of Gothenburg, Sweden)

**Data processing:** Adam Ulfsbo and Leif G. Anderson (University of Gothenburg, Sweden)

**# samples analyzed:** 596

**# stations sampled:** 39

**# CRM analyses:** 70 bottles (Batch 136 and 123)

**Name of data file:** SWERUS-C3 2014 C-system data.csv

**Data file headers:** Station, Year, Month, Day, Hour, Minute, Latitude [degrees_north], Longitude [degrees_east], Pres [dbar], pot.Temp [°C], Salinity [PSS78], Oxygen [$\mu$mol/kg], TA [$\mu$mol/kg], DIC [$\mu$mol/kg], pH-tot-15C

**Preliminary data:** The salinity, temperature and pressure data used are preliminary, i.e., as obtained from the CTD without post-cruise calibration.

## 2  Sampling procedure

Samples were collected in 250 mL Pyrex borosilicate bottles from a 24-Niskin 7 L-bottle CTD rosette according to Dickson et al. (2007) at 39 stations, resulting in a total of 596 samples analyzed, replicate samples excluded. One sample bottle was collected for pH and TA, and one for DIC from each depth. All samples were analyzed on board within hours (no poisoning, e.g., $HgCl_2$). Samples were allowed to reach analysis temperature by being placed in a waterbath of 15°C for $\sim$30 minutes.

## 3  Analytical methods

### 3.1  pH

pH was determined spectrophotometrically (Clayton and Byrne, 1993) using the sulphonephtalien dye, *m*-cresol purple (mCP), as indicator (Liu et al., 2011). Purified mCP was purchased from the laboratory of Robert H. Byrne, University of South Florida, USA. The method is based on the absorption ratio of the indicator at wavelengths 434 and 578 nm using a 1-cm flow cuvette. Each run consisted of three steps; *i)* rinsing of tubing and cuvette with sample (5 mL) *ii)* sample blank (25 mL) and *iii)* sample run (20 mL) including indicator (0.5 mL). The sample was pumped and mixed using a Kloehn pump equipped with a no dead volume syringe. Sample temperature was measured after the cuvette. The spectrophotometer (Agilent 8453) was allowed to warm up ($\sim$1 hour) at start up and Milli-Q water was used as initial instrument blank. Before running a set of samples, the pH of the indicator was measured using a 0.02 cm cuvette. The indicator solution was prepared on several occasions throughout the cruise. A 2 mM indicator solution was prepared by dissolving pre-weighed mCP indicator in 0.5 L filtered seawater of about 34 salinity. The indicator was adjusted to a pH in the same range as the samples, approximately $\pm$ 0.2 pH units, by adding a small volume of 1 M HCl or NaOH. The magnitude of the perturbation of seawater pH caused by the addition of indicator solution was calculated and corrected for using the method described in Chierici et al. (1999). pH data was reported on the total scale at 15°C. Table 1 shows the indicator pH over time (station) used for evaluating the final pH.

Table 1: Indicator pH per station

| Station | pH | Station | pH | Station | pH | Station | pH |
|---------|-------|---------|-------|---------|-------|---------|-------|
| 1 | 8.194 | 94 | 7.725 | 104 | 7.820 | 145 | 7.858 |
| 59 | 7.557 | 95 | 7.738 | 105 | 7.820 | 146 | 7.835 |
| 60 | 7.520 | 96 | 7.738 | 106 | 7.838 | 147 | 7.835 |
| 62 | 7.450 | 97 | 7.753 | 107 | 7.838 | 148 | 7.835 |
| 63 | 7.839 | 98 | 7.788 | 131 | 7.882 | 149 | 7.835 |
| 64 | 7.805 | 99 | 7.798 | 132 | 7.875 | 150 | 7.822 |
| 65 | 7.790 | 100 | 7.798 | 135 | 7.875 | 151 | 7.822 |
| 66 | 7.754 | 101 | 7.798 | 138 | 7.902 | 152 | 7.803 |
| 67 | 7.714 | 102 | 7.820 | 142 | 7.902 | 154 | 7.796 |
| 93 | 7.712 | 103 | 7.820 | 144 | 7.893 | | |

## 3.2 Total alkalinity (TA)

TA was determined by open-cell potentiometric titration with 0.05 M HCl, according to Haraldsson et al. (1997) based on five-point Gran evaulation. The sample was dispensed into a titration vessel from a thermostated pipette of known volume. The titration acid was prepared on board by adding pre-weighed NaCl (75 g) and HCl (1 ampoule 0.1 M for 1000 mL) to a volumetric flask (2 L) diluting with Milli-Q water. New electrodes (Orion 9102AP) were used, which were quality tested in the lab prior to the cruise by their Nernst response, but not on board. The system reports TA in $\mu$mol/L using the nominal acid concentration of 0.05 M. For all samples and CRMs, molar concentrations were converted to molinity ($\mu$mol/kg-SW) using the sample salinity (from the CTD) and the certified salinity, respectively, and the temperature measured at the beginning of each titration. Sample results were then multiplied by the calibration factor from the CRM measurements (measured value divided by the CRM value). No deviant trends were observed regarding acid concentration or performance over time.

## 3.3 Dissolved inorganic carbon (DIC)

DIC was determined using a coulometric titration method (Johnson et al., 1993, 1985, 1987) with a modified Single Operator Multiparameter Metabolic Analyzer (SOMMA) system (coulometer type UIC 5012), the MIDSOMMA system (Mintrop, 2005). The sample is pumped peristaltically into a thermostated pipette, measuring the temperature of overflowing water, and dispensed into a stripper where the sample is acidified and all inorganic carbon species are converted into aqueous $CO_2$. The evolving $CO_2$ is rapidly removed from the stripper by a constant flowing carrier gas ($N_2$, 5.5) via a condenser to the coulometer (UIC model 5012). The titration cell consists of one anodic solution (silver electrode) and one cathodic solution (platinum eletrode). The $CO_2$ reacts in the cathodic cell compartment, also containing a pH indicator, and the solution becomes more transparent. The coulometer subsequently titrates the solution back to its original transmittance. The required amount of charge is proportional to the amount of $CO_2$ reacted and the DIC is readily calculated with known sample volume and density. No current-to-frequency calibration was performed pre- or post-cruise. No highly accurate determination of pipette volume was performed. This was accounted for by the CRM calibration.

## 3.4 Certified reference material

Certified reference material (CRM) was provided by Andrew Dickson (Scripps Institution of Oceanography, San Diego, USA). A total of 70 CRM bottles (Batch 136 and 123) were analyzed during the two legs of the cruise with respect to pH, TA, and DIC. The certificate of analysis is available online at http://cdiac.ornl.gov/oceans/Dickson_CRM/batches.html.

# 4 Analytical quality assessment

A summary of precision and accuracy for all parameters are given in Table 2.

## 4.1 pH

The accuracy of spectrophotometric pH values is difficult to assess, since it relies ultimately on the physicochemical characteristics of the indicator solution, but is mainly set by the equilibrium constants of the indicator. The accuracy, as estimated from internal consistency calculations of analyzed

CRM samples, was 0.006±0.006 (Figure 1 and 2). Spectrophotometer performance was assumed to be sufficient and was not further investigated. Sample temperature was determined from the resistance of an insulated thermistor after passing the cuvette. The system itself was not thermostated and any differences in temperature, although small, between the flow-through cuvette and thermistor contributes to the uncertainty. Since all samples are affected similarly, a more or less constant and small offset should be expected. Internal consistency evaluation of pH values with DIC and TA measurements are discussed in section 5.

A total of 109 duplicates were measured. The overall precision, defined as the absolute mean difference of duplicate samples, was 0.0009±0.0012 (Figure 3). Each duplicate sample was measured from the same sample bottle and the second measurement could possibly be affected by changes in $CO_2$ concentration. However, there was only a small time lapse of ∼5 minutes between measurments, with only minor change in temperature. Triplicates were measured should one of the duplicate measurements seem questionable.

## 4.2 TA

The accuracy is difficult to assess, since the system is calibrated using CRM. Assuming that the CRMs are in the certified range, the accuracy is probably in the same order as the precision. Different stations (days) may show an offset depending on the CRM measuremect (calibration factor) used for calibration. The final choice of calibration factors used, is based on ambient deep water profiles, normalized TA and CO2SYS calculations. The calibration factors used per station for TA and DIC are shown in Figure 4 and 5, respectively. Precision for TA, defined as the average of the differences between duplicate analyses of CRM (Figure 6), was 1.9±2.3 $\mu$mol/kg. In some cases, replicates were measured when questionable results or problems (e.g., incomplete pipette filling, bubbles etc.) were observed. Obvious poor measurements were excluded from the data quality assessment and the dataset. Precision for TA sample duplicates (n=184) was 1.8±2.2 $\mu$mol/kg (Figure 8).

## 4.3 DIC

Different stations (days) may show an offset depending on the CRM measuremet (calibration factor) used for calibration. The final choice of calibration factors used, is based on ambient deep water profiles, normalized TA and CO2SYS calculations. Precision for DIC, defined as the average of the differences between duplicate analyses of CRM (Figure 7), was 1.5±1.8 $\mu$mol/kg. Precision for DIC sample duplicates (n=95) was 2.0±2.7 $\mu$mol/kg (Figure 9).

Table 2: Precision of pH, TA, and DIC for duplicate measurements of samples and CRM.

| Parameter | Sample/CRM | Precision | Accuracy | $n$ |
|---|---|---|---|---|
| pH | CRM | | 0.006±0.006[a] | 81 |
| pH | Sample | 0.0009±0.0012 | | 109 |
| TA | CRM | 1.9±2.3 | | 58 |
| TA | Sample | 1.8±2.2 | | 184 |
| DIC | CRM | 1.5±1.8 | | 58 |
| DIC | Sample | 2.0±2.7 | | 95 |

[a] based on differences between CRM measurements and CRM pH calculated from certified values of
TA, DIC, salinity, silicate, phosphate and constants of Roy et al. (1993) at 15°C on the total scale.

### 4.4 Data set: station and sample availability

DIC data are not available for the Leg 1 stations 1, 59-67. Reported DIC for these stations are calculated from measured pH, TA, silicate, and phosphate using the constants of Millero et al. (2006) at $15^\circ$C on the total scale.

## 5 Internal consistency

The carbonate system can be determined from any two of the four master parameters pH, TA, DIC and $pCO_2$ (partial pressure of $CO_2$), together with known values of relevant stoichiometric dissociation constants and total concentrations (e.g., Anderson et al., 1999; Zeebe and Wolf-Gladrow, 2001). The carbonate system was overdetermined (pH, TA, DIC) and the internal consistency (or thermodynamic consistency) was assessed by comparing measured values to calculated values (from any two of the three determined parameters) using the CO2SYS Matlab program (van Heuven et al., 2011). Different sets of the dissociation constants of carbonic acid ($K_1$ and $K_2$) were used (Table 3).

Table 3: Dissociation constants of carbonic acid ($K_1$ and $K_2$)

| Author | Temperature | Salinity | pH scale |
|---|---|---|---|
| Mehrbach et al. (1979), refit by Dickson and Millero (1987) | 2-35 | 20-40 | Seawater |
| Roy et al. (1993) | 0-45 | 5-45 | Total |
| Millero et al. (2006) | 0-50 | 1-50 | Seawater |

The average mean differences between measured and calculated values were evaluated for pH, TA and DIC. The constants of Millero et al. (2006) showed the best overall internal consistency for all depths, whereas Roy et al. (1993) provided better consistency for the shallower samples. However, the differences were relatively small for the deep waters. The average of the differences between measured and calculated values of pH, TA, and DIC are shown in Table 4 for stations 93-154. The vertical distribution og the internal consistency is exemplified by depth profiles of station 154 appended at the the of this document.

Table 4: Averages of absolute differences between measured and calculated TA, DIC and pH for stations 93-154.

| Constants | All depths | | | Depths < 200 m | | | Depths > 200 m | | |
|---|---|---|---|---|---|---|---|---|---|
| | TA | DIC | pH | TA | DIC | pH | TA | DIC | pH |
| Roy (1993) | 8.20 | 7.93 | 0.022 | 6.68 | 6.51 | 0.019 | 9.52 | 9.17 | 0.024 |
| Mehrbach refit | 6.69 | 6.50 | 0.019 | 7.57 | 7.40 | 0.023 | 5.89 | 5.69 | 0.015 |
| Millero (2006) | 6.56 | 6.37 | 0.018 | 7.78 | 7.60 | 0.023 | 5.56 | 5.28 | 0.014 |

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Roy, R. N., Roy, L. N., Vogel, K. M., Porter-Moore, C., Pearson, T., Good, C. E., Millero, F. J., Campbell, D. M., 1993. The dissociation constants of carbonic acid in seawater at salinities 5 to 45 and temperatures 0 to 45 °C. Marine Chemistry 44 (2-4), 249–267.

van Heuven, S., Pierrot, D., Lewis, E., Wallace, D. W. R., 2011. MATLAB Program Developed for $CO_2$ System Calculations, ORNL/CDIAC-105b. Carbon Dioxide Information Analysis Center Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee, USA.

Zeebe, R. E., Wolf-Gladrow, D. A., 2001. $CO_2$ in seawater: Equilibrium, kinetics, isotopes. Elsevier Oceanography Series 65, 1–346.
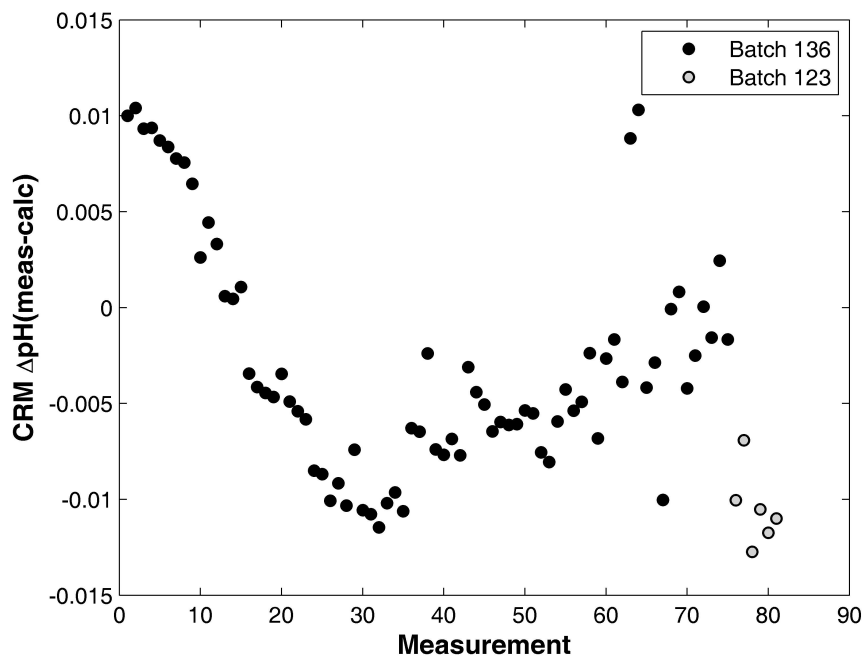
Figure 1: Differences between CRM measurements and CRM pH calculated from certified values of TA, DIC, salinity, silicate, and phosphate using the constants of Roy et al. (1993) at 15°C and total scale.
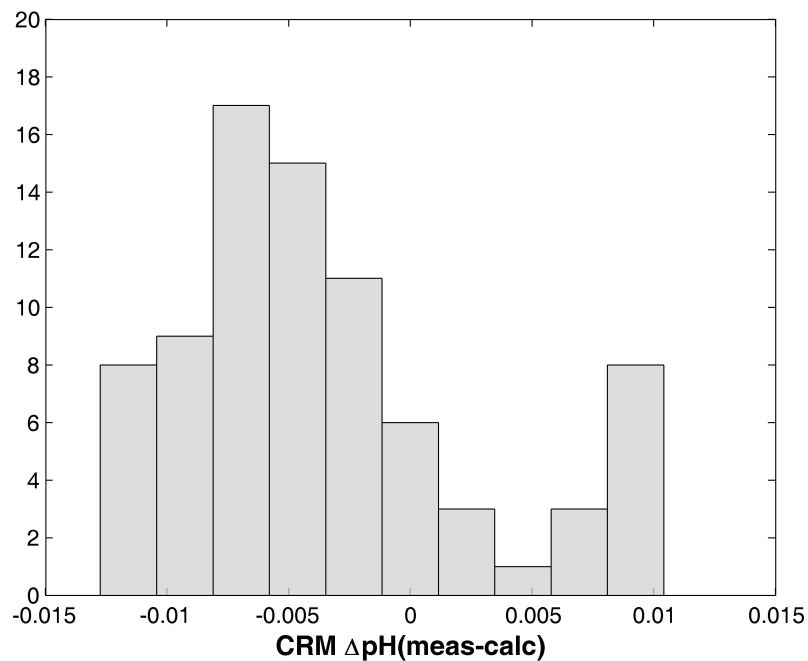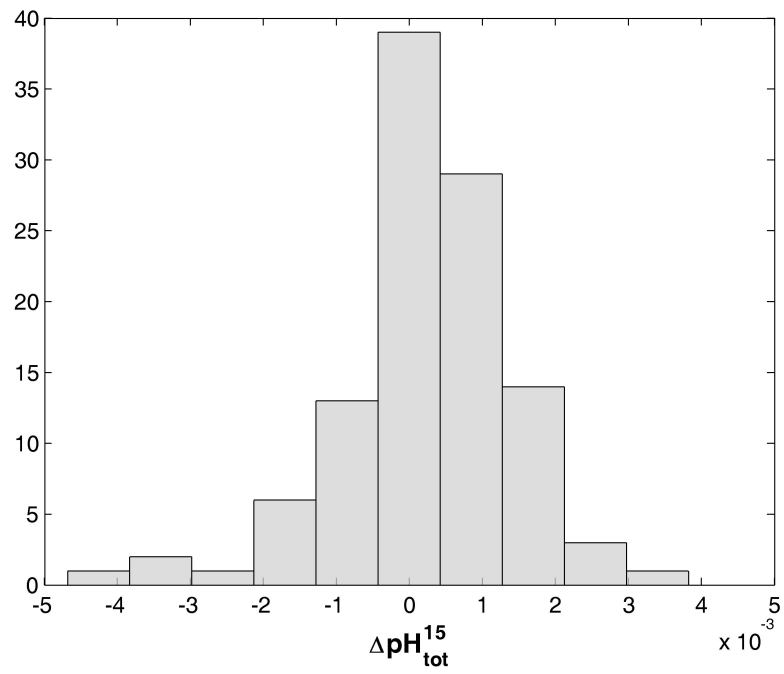


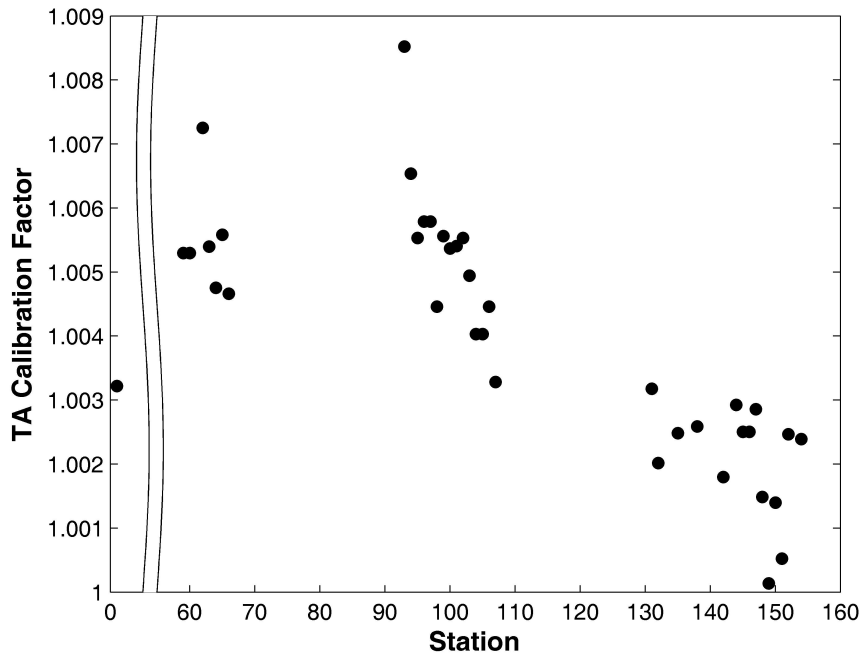Figure 2: Histogram of differences between CRM measurements and CRM pH calculated from certified values of TA, DIC, salinity, silicate, and phosphate using the constants of Roy et al. (1993) at 15°C and total scale.

Figure 3: Histogram of differences between duplicate pH samples.

Figure 4: Calibration factors used for TA per station.
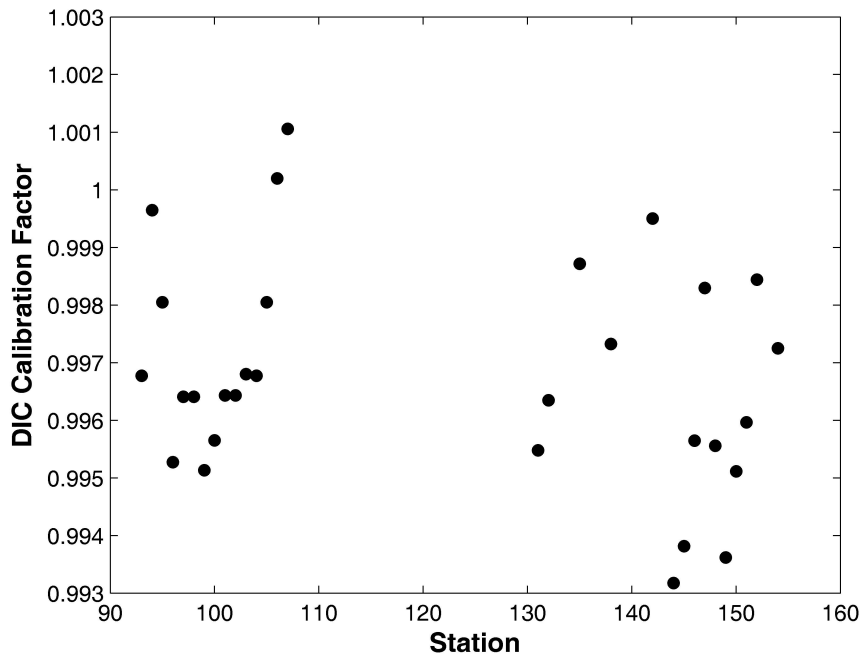


Figure 5: Calibration factors used for DIC per station.

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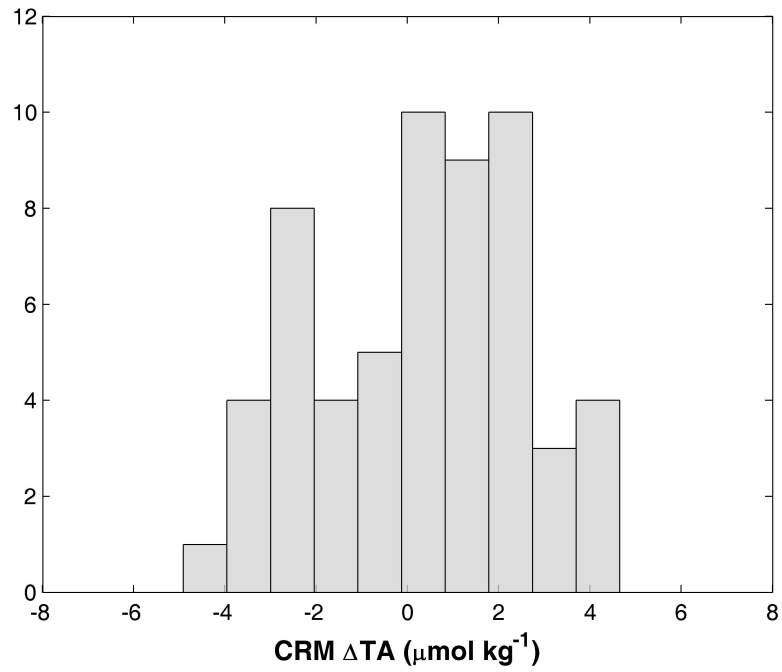
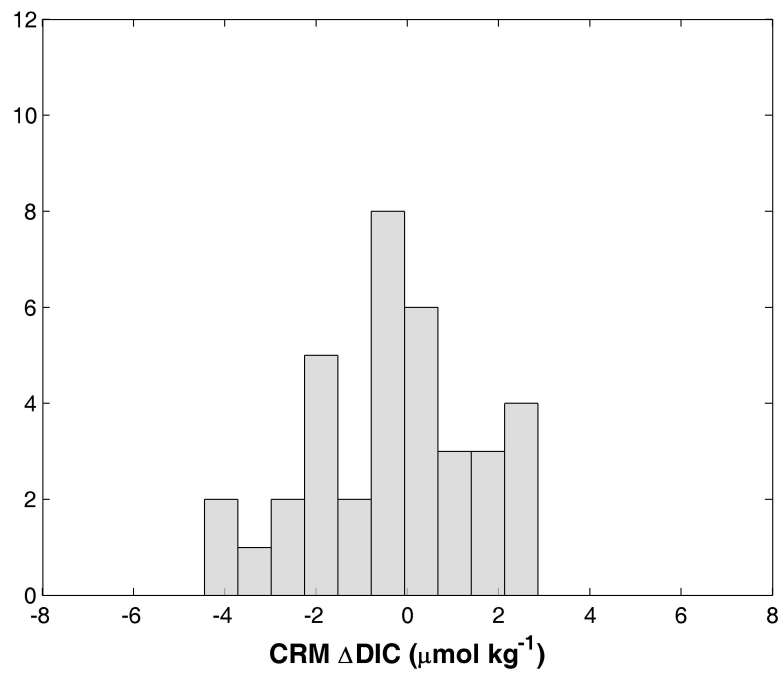Figure 6: Histogram of absolute differences between duplicate TA analyses of the same CRM.



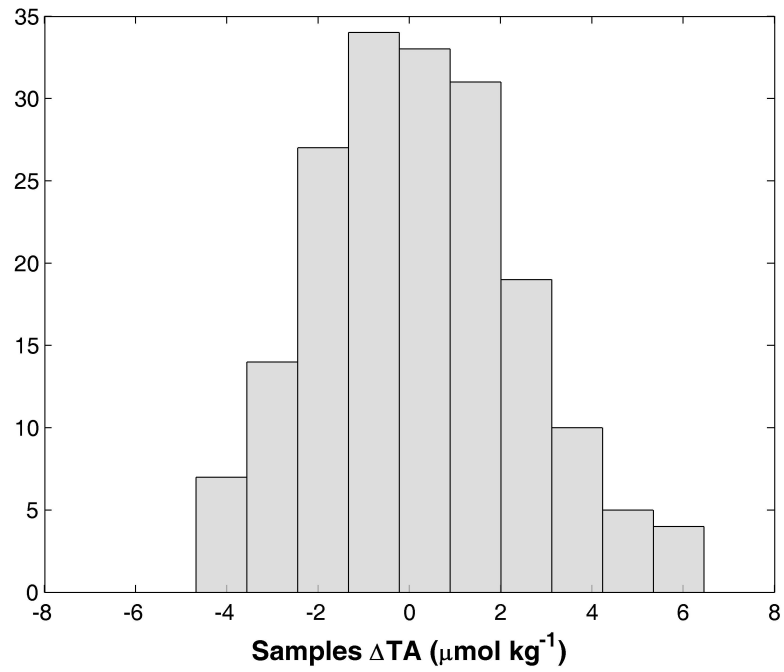Figure 7: Histogram of absolute differences between duplicate DIC analyses of the same CRM.

Figure 8: Histogram of absolute differences between duplicate TA samples.
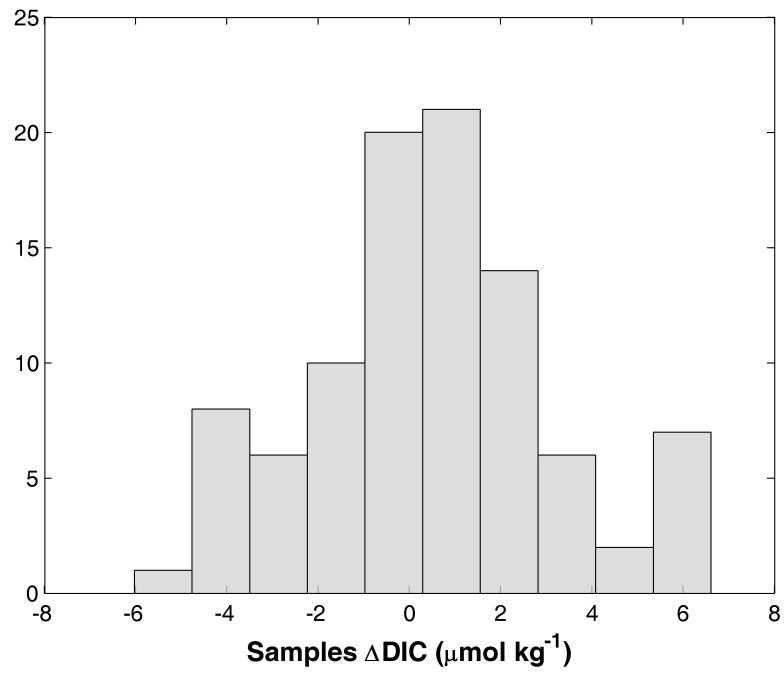


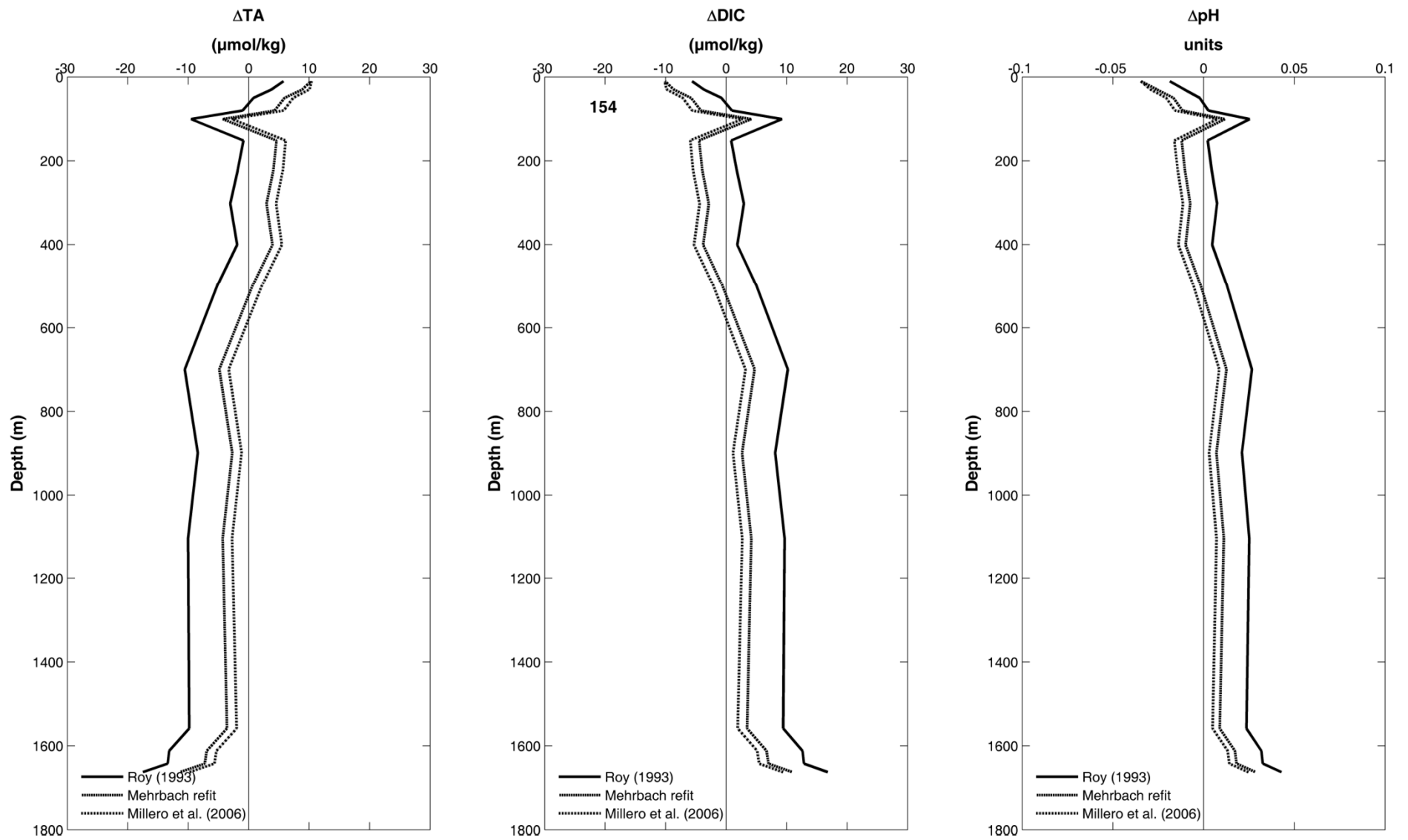Figure 9: Histogram of absolute differences between duplicate DIC samples.

Figure 10: Example of internal consistency for the depth profile of station 154 illustrated by the difference between measured and computed concentrations, the latter using different constants.